PB88-139605

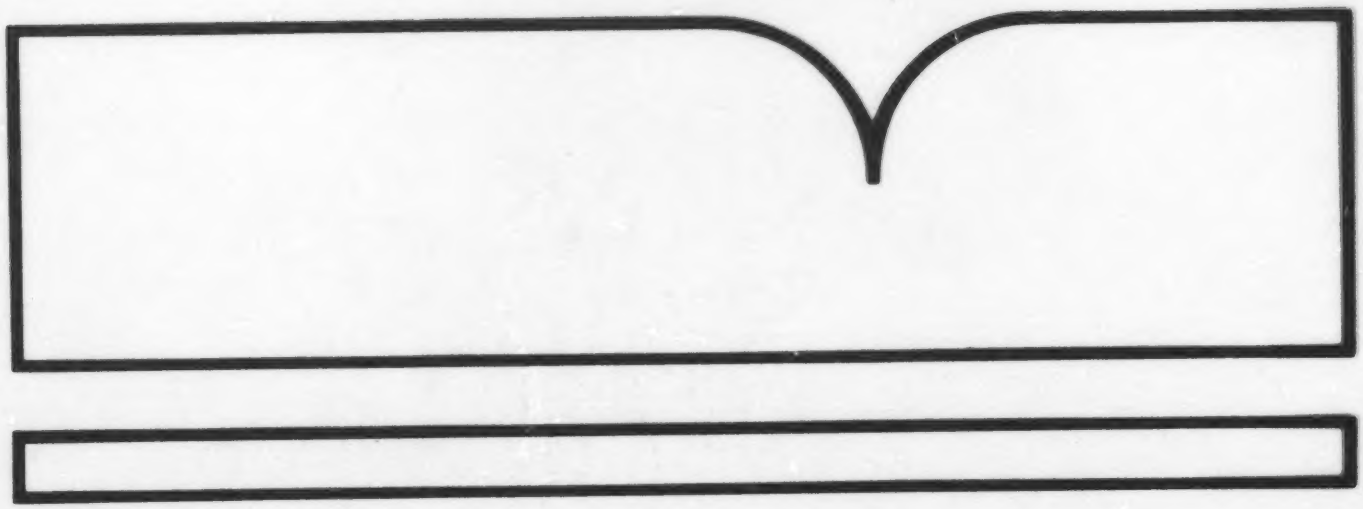
Atmospheric Chemistry of cis - and trans-3-Hexene-2,5-dione

California Univ., Riverside

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

1985



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1. REPORT NO. EPA/600/J-85/506	3. RECIPI PB88-139605
4. TITLE AND SUBTITLE **Atmospheric Chemistry of *cis*- and *trans*-3-Hexene-2,5-dione** (Journal Version)	5. REPORT DATE 1985
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) E. C. Tuazon, R. Atkinson, and W. P. L. Carter	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Statewide Air Pollution Research Center University of California Riverside, CA 92521	10. PROGRAM ELEMENT NO. CDWA1A/01-1463 (FY-85) 11. CONTRACT/GRANT NO. Cooperative Agreement 810966
12. SPONSORING AGENCY NAME AND ADDRESS Atmospheric Sciences Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	13. TYPE OF REPORT AND PERIOD COVERED Journal Article (5/84-10/84) 14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES Environ. Sci. Technol., 19(3):265-269, March 1985	

16. ABSTRACT

The atmospheric chemistry of cis- and trans-2-hexene-2, 5-dione has been studied. These isomers have been postulated as products of the atmospheric degradation of aromatic hydrocarbons. The photolysis of these isomers and their reaction with OH and O_3 were investigated. In addition to determining rate constants for these processes, the products of these reactions were also identified. The atmospheric implications of these results are discussed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

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18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED 20. SECURITY CLASS (This page) UNCLASSIFIED	21. NO. OF PAGES 7 22. PRICE PC 9.95 / MF 6.95

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

EPA/600/J-85/506
JOURNAL ARTICLE

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Atmospheric Chemistry of *cis*- and *trans*-3-Hexene-2,5-dione

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■ As part of an investigation of the atmospheric chemistry of the unsaturated 1,4-dicarbonyls, which have been postulated and experimentally observed to be formed as ring cleavage products during the atmospheric degradation of aromatic hydrocarbons, we have studied the photolyses of *cis*- and *trans*-3-hexene-2,5-dione and the reactions of these isomers with OH radicals and O_3 at 298 ± 2 K. The rate constants for the cis and trans isomers were respectively $(1.8 \pm 0.2) \times 10^{-18}$ and $(8.3 \pm 1.2) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} for reaction with O_3 and $(6.3 \pm 0.6) \times 10^{-11}$ and $(5.3 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for reaction with OH radicals. Under our experimental conditions, the photolysis rates of the cis and trans isomers were respectively 0.048 ± 0.019 and 0.076 ± 0.019 times the rate of photolysis of NO_2 and 1.3 ± 0.5 and 2.1 ± 0.5 times the rate of photolysis of biacetyl. Methylglyoxal and formaldehyde were observed to be among the products of the reaction with O_3, but methylglyoxal was not detected as a product of the reaction with OH radicals. In the photolysis experiments, photoisomerization to the corresponding geometric cis or trans isomer accounted for ≳80% of the total photolysis rate, with a photoequilibrium [trans]/[cis] ratio of 0.55 ± 0.05 being achieved under our irradiation conditions. This is the first study of the atmospheric chemistry of this class of compounds, and the atmospheric implications are discussed.

Introduction

The unsaturated 1,4-dicarbonyls such as *cis*-2-butene-1,4-dial (CHOCH=CHCHO), *cis*-2-pentene-1,4-dione (CH_3COCH=CHCHO), and *cis*-3-hexene-2,5-dione (CH_3COCH=$CHOCH_3$) have been postulated to be important ring-cleavage products in the NO_x–air photooxidations of the aromatic hydrocarbons (*1*–*3*) and of hydroxy-substituted aromatics (*1*). Recently the formation of 2-butene-1,4-dial from the NO_x–air photooxidation of toluene (*4*) and of 3-hexene-2,5-dione from the NO_x–air photooxidations of *p*-xylene and 1,2,4-trimethylbenzene (*5*) has been reported, though in low yields.

However, to date no data are available concerning the kinetics, mechanisms, and products of the degradation pathways of these unsaturated 1,4-dicarbonyls under atmospheric conditions, and hence, the involvement of these organics in the atmospheric photooxidations of the aromatic hydrocarbons cannot be accurately assessed. Since the major loss processes for these unsaturated 1,4-dicarbonyls under atmospheric conditions are expected (*6*) to be via photolysis and reaction with OH radicals and with O_3, in this work we have determined these rate constants for *cis*- and *trans*-3-hexene-2,5-dione in 1 atm of air at 298 ± 2 K.

Experimental Section

Photolysis and OH Radical Reactions. The OH radical rate constants were determined by using a relative rate method (*7*), and the techniques used for the determination of these relative OH radical rate constants and of the photolysis rates were essentially identical with those described in our previous study of the atmospheric chemistry of the α-dicarbonyls glyoxal and methylglyoxal (*8*).

Hydroxyl radicals were generated by the photolysis of methyl nitrite in air at ≳300 nm, at part-per-million concentrations (1 ppm = 2.38×10^{13} molecule cm^{-3} at 735 torr total pressure and 298 K).

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

In order to minimize the formation of O_3 during these irradiations, NO was included in the reaction mixtures. In the presence of *cis*- or *trans*-3-hexene-2,5-dione (*cis*- or *trans*-HD) and a reference organic (propene in this study) the OH radicals can, besides reacting with CH_3ONO, NO, NO_2, and the organic reaction products, react with these organics:

$$OH + \textit{cis}\text{- or } \textit{trans}\text{-HD} \rightarrow \text{products} \quad (1)$$

$$OH + \text{propene} \rightarrow \text{products} \quad (2)$$

Additionally, the 3-hexene-2,5-dione isomers can also photolyze:

$$\textit{cis}\text{- or } \textit{trans}\text{-HD} + h\nu \rightarrow \text{products} \quad (3)$$

Under the experimental conditions employed, reactions with O_3 and $O(^3P)$ atoms were essentially negligible (see below) and hence, as previously derived (*8*)

$$\frac{1}{t - t_0} \ln \left(\frac{[\textit{cis}\text{- or } \textit{trans}\text{-HD}]_{t_0}}{[\textit{cis}\text{- or } \textit{trans}\text{-HD}]_t} \right) = k_3 + \frac{k_1}{k_2(t - t_0)} \ln \left(\frac{[\text{propene}]_{t_0}}{[\text{propene}]_t} \right) \quad (I)$$

where $[\textit{cis}\text{- or } \textit{trans}\text{-HD}]_{t_0}$ and $[\text{propene}]_{t_0}$ are the concentrations of *cis*- or *trans*-3-hexene-2,5-dione and propene, respectively, at time t_0, $[\textit{cis}\text{- or } \textit{trans}\text{-HD}]_t$ and $[\text{propene}]_t$ are the corresponding concentrations at time t, and k_1, k_2, and k_3 are the rate constants for reactions 1–3, respectively. Hence, plots of $(t - t_0)^{-1} \ln ([\textit{cis}\text{- or } \textit{trans}\text{-HD}]_{t_0}/[\textit{cis}\text{- or } \textit{trans}\text{-HD}]_t)$ vs. $(t - t_0)^{-1} \ln ([\text{propene}]_{t_0}/[\text{propene}]_t)$ should yield straight lines of slope k_1/k_2 and intercept k_3. The OH radical concentrations during these irradiations were varied by varying the initial CH_3ONO concentrations, and irradiations were also carried out in the absence of CH_3ONO to minimize the OH radical concentrations.

Irradiations of CH_3ONO/NO/*cis*- or *trans*-3-hexene-2,5-dione/propene/air or NO/*cis*- or *trans*-3-hexene-2,5-dione/propene/air mixtures were carried out in the SAPRC 5800-L Teflon-coated evacuable, thermostated environmental chamber, equipped with a 25-kW xenon arc solar simulator (*9*). This chamber was also equipped with a multiple-reflection optical system, interfaced to a Fourier transform infrared (FT-IR) absorption spectrometer. As in our previous study concerning the α-dicarbonyls (*8*), the radiation from this solar simulator was filtered by passage through a 0.64-cm Pyrex pane to eliminate radiation below ~300 nm. The resulting spectral distribution, which approximated that of the lower tropospheric solar spectrum, was essentially identical with that reported by Plum et al. (*8*). The absolute light intensity was monitored by de-

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termining the photolysis rates of NO_2 (in N_2) and of biacetyl (*8*). These photolysis rates under the irradiation conditions employed in this study were 2.1×10^{-3} s^{-1} for NO_2 and 7.6×10^{-5} s^{-1} for biacetyl.

The *cis*- and *trans*-3-hexene-2,5-dione, propene, and certain reaction products (e.g., methylglyoxal and formaldehyde) were quantitatively monitored prior to and during these irradiations by FT-IR absorption spectroscopy, using a path length of 62.9 m and a spectral resolution (unapodized) of 1 cm^{-1}. The reactants were monitored at the following absorption frequencies: *cis*-3-hexene-2,5-dione, 1170 and 1720 cm^{-1}; *trans*-3-hexene-2,5-dione, 1250 and 1705 cm^{-1}; propene, 912 cm^{-1}.

The initial concentrations of the reactants in these irradiations were the following (in molecule cm^{-3} units): *cis*-3-hexene-2,5-dione, $\sim 2.4 \times 10^{14}$; *trans*-3-hexene-2,5-dione, $\sim 1.2 \times 10^{14}$; NO, $\sim (1.2–2.1) \times 10^{14}$; CH_3ONO (when present), $(1.2–2.4) \times 10^{-14}$; propene, $\sim 2.4 \times 10^{14}$. Synthetic air (80% N_2 + 20% O_2) was used as the diluent gas.

Ozone Reactions. The technique used for the determination of the ozone reaction rate constants was based (*10*) upon observing the enhanced rate of ozone decay in the presence of *cis*- or *trans*-3-hexene-2,5-dione. Under these conditions the processes removing O_3 were

$$O_3 + \text{wall} \rightarrow \text{loss of } O_3 \qquad (4)$$

$$O_3 + \textit{cis}\text{- or } \textit{trans}\text{-HD} \rightarrow \text{products} \qquad (5)$$

Under conditions where the 3-hexene-2,5-dione concentrations were in large excess over the initial O_3 concentration ([*cis*- or *trans*-HD]/$[O_3]_{init} \geq 10$), then (*8*, *10*)

$$\frac{-\text{d ln } [O_3]}{dt} = k_4 + k_5[\textit{cis}\text{- or } \textit{trans}\text{-HD}] \qquad (II)$$

Hence, plots of the O_3 decay rate, $-\text{d ln } [O_3]/dt$, vs. the *cis*- or *trans*-3-hexene-2,5-dione concentration should yield straight lines of slope k_5 and intercept k_4.

As described previously (*8*, *10*), reactions were carried out in a ~175-L Teflon bag. This reaction bag was initially divided into two subchambers, with O_3 being injected into one subchamber and the *cis*- or *trans*-3-hexene-2,5-dione into the other. The reactions were initiated by removing the bag divider and rapidly mixing the contents of the bag by pushing down on alternate sides of the entire bag for ~1 min. Initial O_3 concentrations after mixing were $\lesssim 2 \times 10^{13}$ molecule cm^{-3}, and after mixing of the reactants, the O_3 concentrations were monitored as a function of time by a Monitor Labs Model 8410 chemiluminescence ozone analyzer. Background O_3 decay rates in the absence of *cis*- or *trans*-3-hexene-2,5-dione, k_4, were determined periodically during this study.

Materials and Methods

trans-3-Hexene-2,5-dione was prepared by oxidation of 2,5-hexanedione with selenious acid (*11*). The faint yellow needles of this isomer, which were obtained by recrystallization in petroleum ether and then in hexane, showed NMR signals at $\delta(CDCl_3) = 2.39$ (s, 6 H) and 6.80 (s, 2 H). *cis*-3-Hexene-2,5-dione was prepared from 2,5-dimethoxy-2,5-dimethyl-2,5-dihydrofuran as described by Levisalles (*12*). After separation by vacuum distillation, the yellowish liquid showed NMR peaks at $\delta(CDCl_3) = 2.29$ (s, 6H) and 6.34 (s, 2 H). The vapor-phase FT-IR infrared spectra of these two 3-hexene-2,5-dione isomers, covering the region 700–1900 cm^{-1}, are shown in Figure 1.

For one experiment conducted in the ~175-L Teflon bag, a known vapor pressure of the *cis*-3-hexene-2,5-dione was measured into a calibrated 5-L Pyrex bulb, and the sample was then flushed into the chamber by a stream of

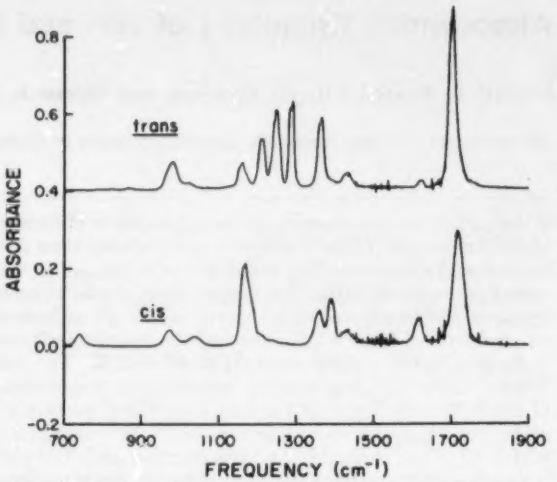


Figure 1. Vapor-phase FT-IR absorption spectra (700–1900 cm^{-1}) of *cis*- and *trans*-3-hexene-2,5-dione: partial pressure of each isomer in 1 atm of air = 3.8 mtorr; path length = 62.9 m; absorbance unit in base 10. The trans spectrum has been offset by 0.4 absorbance unit for clarity.

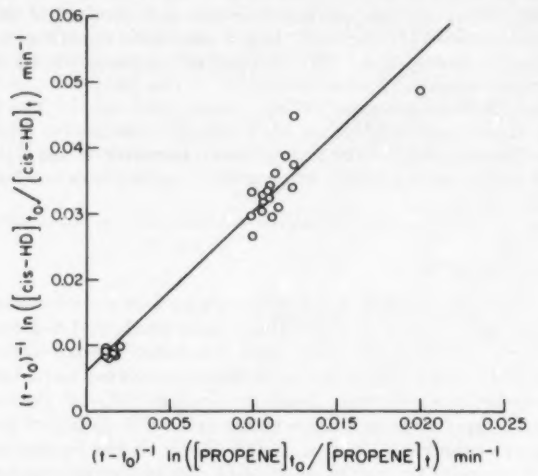


Figure 2. Plot of eq I for *cis*-3-hexene-2,5-dione.

N_2. For the remaining experiments carried out in the ~175-L Teflon bag and for the larger amounts required in the 5800-L chamber, weighed amounts of the solid trans and liquid cis isomers were flushed, with heating, into the chamber by N_2 gas.

Methyl nitrite was prepared by collecting the vapors generated by dropwise addition of 50% H_2SO_4 to a saturated solution of $NaNO_2$ in CH_3OH (*13*). Ozone was produced in a Welsbach T-408 generator at a precalibrated voltage and input flow of high purity O_2 (Liquid Carbonic, 99.995%) and collected either in a gas syringe or a calibrated Pyrex bulb. Commercial samples of NO (Matheson, ≥99.0%) and propene (Matheson, ≥99.0%) were used without further purification.

Results

Photolysis and OH Radical Reactions. A series of irradiations of $CH_3ONO/NO/$*cis*- or *trans*-3-hexene-2,5-dione/propene/air and NO/*cis*- or *trans*-3-hexene-2,5-dione/propene/air mixtures were carried out, with propene serving as the reference organic. The data from these irradiations are plotted in accordance with eq I in Figures 2 and 3. It can be seen from these figures that the data

Table I. Rate Constant Ratios k_1/k_2 and Rate Constants for the Reaction of *cis*- and *trans*-3-Hexene-2,5-dione with OH Radicals (k_1), O_3 (k_3), and Photolysis (k_3)

3-hexene-2,5-dione isomer	OH radical reaction		O_3 reaction	photolysis
	k_1/k_2[a]	$10^{11}k_1$, cm^3 molecule^{-1} s^{-1}[a,b]	$10^{18}k_3$, cm^3 molecule^{-1} s^{-1}[c]	10^4k_3, s^{-1}[a,d]
cis	2.40 ± 0.23	6.3 ± 0.6	1.8 ± 0.2	1.0 ± 0.4
trans	2.02 ± 0.09	5.3 ± 0.3	8.3 ± 1.2	1.6 ± 0.4

[a] Indicated errors are two least-squares standard deviations. [b] Placed on an absolute basis by using a rate constant for the reaction of OH radicals with propene of 2.63×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K (*14*). [c] Error limits are two least-squares standard deviations of the slopes of the plots shown in Figure 5 combined with estimated 10% error limits for the 3-hexene-2,5-dione concentrations. [d] At NO_2 and biacetyl photolysis rates of 2.1×10^{-3} s^{-1} and 7.6×10^{-6} s^{-1}, respectively.

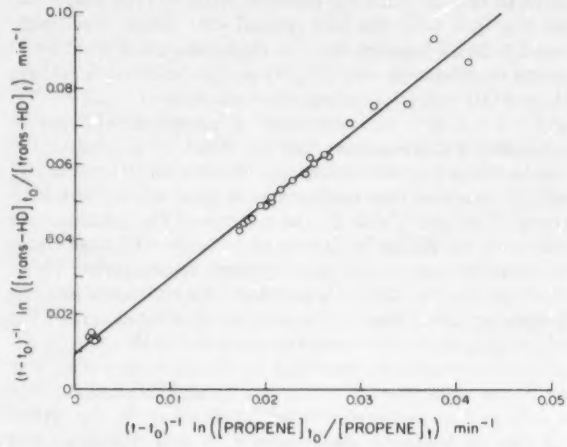


Figure 3. Plot of eq I for *trans*-3-hexene-2,5-dione.

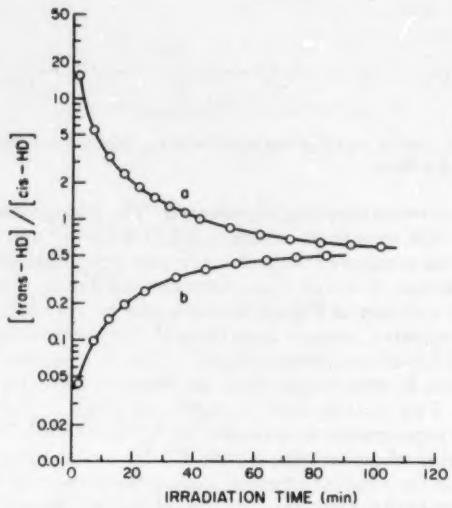


Figure 4. Plot of the [*trans*-3-hexene-2,5-dione]/[*cis*-3-hexene-2,5-dione] ratio, as a function of the irradiation time. (a, starting with a pure trans isomer; b, starting with a pure cis isomer).

obtained yield reasonably good straight line plots. The rate constant ratios k_1/k_2 and the rate constants k_3 obtained from the slopes and intercepts, respectively, of these plots by least-squares analyses are given in Table I.

On the basis of the observed maximum O_3 yields during these irradiations ($\leq 3.6 \times 10^{12}$ molecule cm^{-3}), the OH radical concentrations derived from the decay rates of propene [$\sim(1\text{–}2) \times 10^7$ molecule cm^{-3}], and the O_3 and OH radical rate constants derived here, the O_3 reactions can be estimated to contribute $\lesssim 5\%$ of the overall disappearance rates for both the 3-hexene-2,5-dione isomers and propene during these irradiations. Similarly, on the basis of the NO_2 photolysis rates, the observed NO_2 concentrations, and estimated reaction rate constants of $\sim 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for the reaction of O(^{3}P) atoms with the *cis*- and *trans*-3-hexene-2,5-dione isomers [estimated by methods analogous to those used by Atkinson and Lloyd (*6*) for the corresponding O_3 and OH radical reaction rate constants], the contribution of O(^{3}P) atom reactions can be calculated to account for $\lesssim 10\%$ of the overall 3-hexene-2,5-dione and propene disappearance rates. Hence, it is evident that the observed disappearance rates of the 3-hexene-2,5-dione isomers and of propene in these irradiations are essentially totally due to reaction with the OH radical.

The rate constant ratios k_1/k_2 for *cis*- and *trans*-3-hexene-2,5-dione can be placed on an absolute basis by using a literature rate constant k_2 for the reaction of OH radicals with propene. On the basis of the value of $k_2 = 2.63 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} derived by Atkinson and Aschmann (*14*), the rate constants k_1 given in Table I are obtained.

Absorption bands due to the products arising from the photolysis of the 3-hexene-2,5-dione isomers and their reaction with OH radicals were evident in the infrared spectra after subtraction of the absorption bands of known components. Unfortunately, these products are as yet unidentified. In particular, the expected formation of methylglyoxal (see Discussion) at levels above the detection limit of $\sim 6 \times 10^{12}$ molecule cm^{-3} was not observed during these irradiations.

For the irradiations carried out in the absence of CH_3ONO, during which the predominant loss process for the 3-hexene-2,5-dione isomers was due to photolysis, it was observed that photoisomerization of the cis isomer to the trans isomer occurred, and vice versa. Associated experiments, each starting with a nearly pure cis or trans isomer, showed (Figure 4) that an equilibrium [*trans*-HD]/[*cis*-HD] ratio of 0.55 ± 0.05 was approached under the irradiation conditions employed and that the cis $\rightleftarrows$ trans photoisomerization accounted for $\gtrsim 80\%$ of the observed loss rate for each isomer under these conditions. Unfortunately, due to the low vapor pressures of the *cis*- and *trans*-3-hexene-2,5-dione isomers (~ 0.2 and ~ 0.08 torr, respectively, at 296 K) and the unavailability of a long-path ultraviolet spectrophotometer, absorption spectra in the wavelength region $\gtrsim 290$ nm could not be obtained. However, these isomers must certainly absorb at wavelengths $\gtrsim 290$ nm, as indicated by the yellow coloration of the pure liquid or solid compounds and by their photolysis in this wavelength region. This is totally consistent with the reported spectrum of *cis*-butene-1,4-dial in octane solution (*15*).

Ozone Reactions. Ozone decays were monitored in the presence of varying concentrations of *cis*- and *trans*-3-hexene-2,5-dione. In all cases these O_3 decays were, within

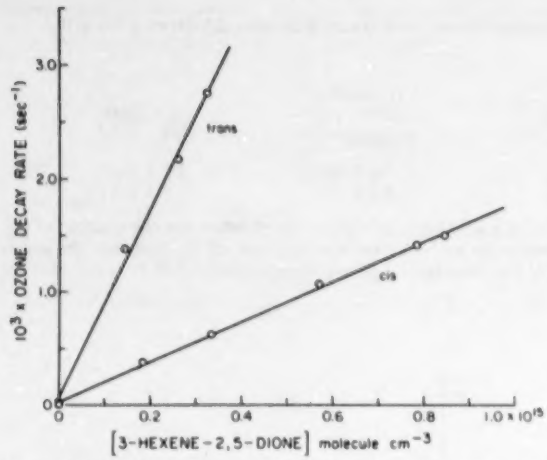


Figure 5. Plot of eq II for the reaction of O_3 with *cis*- and *trans*-3-hexene-2,5-dione.

the experimental errors, exponential. The background O_3 decay rates were in the range (1.3–2.7) × 10^{-5} s^{-1} and were negligible compared with the O_3 decay rates observed in the presence of *cis*- or *trans*-3-hexene-2,5-dione. Plots of eq II are shown in Figure 5, and it can be seen that the O_3 decay rates increase linearly with the *cis*- or *trans*-3-hexene-2,5-dione concentrations. The O_3 reaction rate constants k_3 determined from the slopes of these plots in Figure 5 by least-squares analyses are given in Table I.

Two experiments were conducted in the SAPRC 5800-L evacuable chamber employing FT-IR spectroscopy to monitor the products formed during these reactions. In the first experiment, the reaction of *trans*-3-hexene-2,5-dione (1.4 × 10^{14} molecule cm^{-3}) with excess O_3 (3 × 10^{14} molecule cm^{-3}) showed complete consumption of the trans isomer after 20 min, with yields of methylglyoxal and formaldehyde of 47% and 27%, respectively. In a further experiment, the reaction of the cis isomer (2.4 × 10^{14} molecule cm^{-3}) with O_3 (1.2 × 10^{14} molecule cm^{-3}) resulted in 30% of the cis compound reacting after 30 min, with the yields of methylglyoxal and formaldehyde being 52% and 36%, respectively.

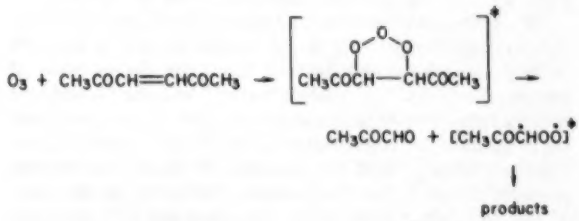
In the above reactions of *trans*- and *cis*-hexene-2,5-dione with O_3, another major, and as yet unidentified, product was formed, which was common to both isomers. The infrared spectral features of this unknown product include broad overlapping absorptions at 1700–1800 cm^{-1} and bands at 1368, 1200, 1102, 1048, and 997 cm^{-1}. Further comparison of the product spectra of the cis and trans isomers indicates the formation of additional product(s) unique to each isomer (e.g., a 1626-cm^{-1} band for the cis isomer and a 1232-cm^{-1} band for the trans isomer).

Discussion

The kinetic measurements and the products determined in this study yield valuable data concerning the atmospheric chemistry of the *cis*- and *trans*-3-hexene-2,5-dione isomers. Under atmospheric conditions, with assumed concentrations of ~7 × 10^{11} molecule cm^{-3} of O_3 (*16*) and ~1 × 10^6 cm^{-3} of OH radicals (*17*), and with a noontime NO_2 photolysis rate constant of ~(8–9) × 10^{-3} s^{-1} (*18*), the lifetimes for the cis isomer can be calculated to be ~8 days for reaction with O_3, ~6 h for reaction with OH radicals, and ~30–35 min for photolysis, with similar lifetimes for the trans isomer. While these calculations imply that photolysis will be the major loss process of *cis*- or *trans*-3-hexene-2,5-dione, the observation that photoisomerization to the corresponding trans or cis isomer accounts for ≥80% of the overall observed 3-hexene-2,5-dione photolyses rates shows that the photodissociation lifetimes of the 3-hexene-2,5-dione isomers are ≥3 h. Hence, reaction with OH radicals will be competitive with, or possibly more important than, photodissociation.

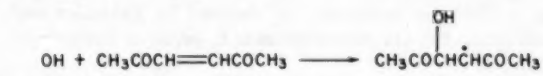
Approximate a priori predictions of the rate constants for the addition of O_3 or OH radicals to the carbon–carbon double bond in 3-hexene-2,5-dione can be made (*6*, *19*) on the basis of the corresponding rate constants for ethene and methyl vinyl ketone ($CH_3COCH{=}CH_2$). On the basis of the literature data for these reactions (*6*, *19*), the CH_3CO group is electron donating, with a substituent effect (relative to H–) of ~2.7 for reaction with O_3 (*19*) and ~2.5 for reaction with the OH radical (*6*). Since the 3-hexene-2,5-dione isomers involve replacement of the two H atoms on ethene by two CH_3CO groups, room temperature O_3 and OH radical reaction rate constants of ~1.3 × 10^{-17} and ~5.3 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively, can be estimated if it is assumed that the effects of disubstitution can be treated as multiplicative. While this estimated OH radical reaction rate constant is in good agreement with those observed (Table I), the estimated O_3 reaction rate constants are higher by factors of ~7 and ~1.5 than those observed for the cis and trans isomers, respectively. These discrepancies in these O_3 reaction rate constants are not surprising, since there are a number of other examples for which this estimation technique overestimates the O_3 reaction rate constants, especially for the cis isomer (*19*). For a further discussion of estimated O_3 and OH radical rate constants for other unsaturated 1,4-dicarbonyls, the review articles of Atkinson and Carter (*19*) and Atkinson and Lloyd (*6*) should be consulted.

The reactions with O_3 are expected, by analogy with the corresponding reaction for the alkenes (*6*, *19*), to proceed via initial addition of O_3 to the olefinic double bond, with subsequent reactions as follows:

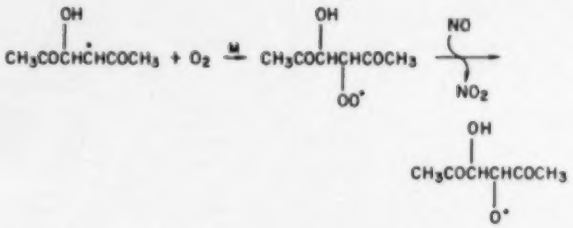


Since the products ultimately formed from the initially energy-rich $[CH_3\dot{C}OCHO\dot{O}]^*$ biradical are not generally known (*19*) and may in fact include methylglyoxal itself, the methylglyoxal yield would be expected to be unity or higher, a factor of ~2 higher than observed. The low yields of methylglyoxal observed may be due to consumption of the 3-hexene-2,5-dione isomers by OH radicals formed from secondary reactions of the energy-rich biradicals, to secondary reactions of the methylglyoxal formed, or (less likely) due to the reaction of O_3 with the 3-hexene-2,5-dione isomers occurring via pathways other than that shown above.

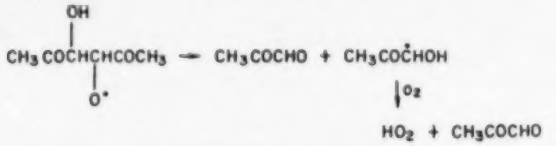
For the OH radical reactions, it is expected (*6*) that the initial reaction involves OH radical addition to the carbon–carbon double bond



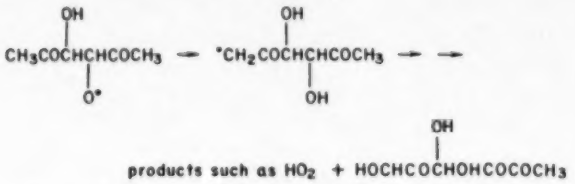
with the adduct reacting rapidly with O_2, and then with NO, to form an alkoxy radical:



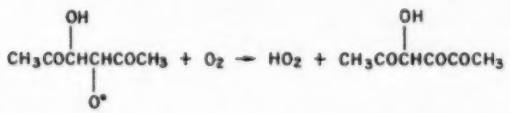
On the basis of analogous reaction systems, it would be expected a priori that decomposition of this alkoxy radical to CH_3COCHO and $CH_3\dot{C}OHOH$ would predominate (*6*):



However, the observation that methylglyoxal is not a major product of this OH radical reaction suggests that other reaction pathways dominate. For instance, this alkoxy radical can undergo isomerization



or react with O_2



with current estimates of the rates of alkoxy radical reactions (*6*) suggesting that isomerization is likely to be the more important of these latter two processes.

In conclusion, this study has provided, for the first time, data concerning the atmospheric reactions of a representative unsaturated 1,4-dicarbonyl. A better understanding of their reactions is essential before their role in the atmospheric degradation of aromatic hydrcarbons can be assessed. It is, however, obvious that further studies of the gas-phase reactions of this class of organic compounds are required before a complete understanding of their atmospheric chemistry is known.

Acknowledgments

We thank William D. Long for assistance in conducting the chamber experiments, Sara M. Aschmann for carrying out the O_3 rate constant determinations, and Jong Kim for help in preparation of the *cis*- and *trans*-3-hexene-2,5-dione isomers.

Registry No. *cis*-HD, 17559-81-8; *trans*-HD, 820-69-9; OH, 3352-57-6; O_3, 10028-15-6; methylglyoxal, 78-98-8; formaldehyde, 50-00-0.

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Received for review July 11, 1984. Accepted October 16, 1984. This work was financially supported by U.S. Environmental Protection Agency Cooperative Agreement CR810964-01 (Project Officer, Marcia C. Dodge). Although this work was funded by the U.S. Environmental Protection Agency, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

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